Polymerization of acrylamide initiated with Ce(IV)- and KMnO₄-mercaptosuccinic acid redox systems in acid-aqueous medium

C. Özeroglu*, S. Sezgin*

Department of Chemistry, Faculty of Engineering, Istanbul University, 34320 Avcilar Istanbul, Turkey

Abstract. By using mercaptosuccinic acid-cerium(IV) sulfate and mercaptosuccinic acid-KMnO₄ redox systems in acid aqueous medium, the polymerization of acrylamide monomer was performed at room temperatures. Water soluble acrylamide polymers which contain mercaptosuccinic acid end-groups were synthesized. The dependence of polymerization yield and the molecular weight of polymer on the initiator concentration($n_{MSA} = n_{Ce(IV)}$) at different acid concentrations, polymerization time, temperature, and concentration of sulfuric acid was investigated. The decrease in the initiator concentration resulted in an increase in the molecular weight but a decrease in the yield. The increase of reaction temperature from 20 to 60°C resulted in an increase in the molecular weights and slight decrease of the yield of polymer. Cerium and manganese ions are reduced to Ce(III) and Mn(II) ions respectively in polymerization reaction. The existence of Ce(III) ion bound to polymer was investigated by UV-visible spectrometry and fluorescence measurements. The amount of Mn(II) which is incorporated to the polymer was determined.

Keywords: polymer synthesis, molecular engineering, mercaptosuccinic acid, cerium(IV) sulfate, redox polymerization, acrylamide

1. Introduction

KMnO₄ and ceric salts-(organic) reducing agent systems in acid-aqueous medium were used for polymerization of vinyl monomers. These methods have also been used for the preparation of graft copolymers of vinyl monomers such as acrylonitrile, methylmethacrylate, acrylic acid or acrylamide [1–15]. In previous studies, water soluble polymers containing amine, hydroxyl, carboxyl, dicarboxylic or amino tri(methylene phosphonic acid) end groups were synthesized by using redox initiator systems [16–23]. The initiator system, especially using mercaptosuccinic acid was used firstly in this study. Unlike other reducing agents used in most previous studies, mercaptosuccinic acid contains S–H group. The formation of –S˙ radicals are more probable at low temperatures, because of low bonding energy of S–H bond. This gives advantages us to save energy in polymerization process and to obtain polymer with low degree of branching. Moreover if mercaptosuccinic acid is used as a reducing agent, polyacrylamide bearing mercaptosuccinic acid end groups is synthesized. Because of on the presence of this functional group in the polymer, it may also find some practical applications in various industries.

In the present communication, the polymerization of acrylamide monomer initiated by cerium(IV) sulfate-mercaptosuccinic acid and potassium permanganate-mercaptosuccinic acid redox systems was investigated at room temperatures. The effects of initiator concentration($n_{MSA} = n_{Ce(IV)}$), polymer-

---

ization time, temperature, the concentration of sulfuric acid on the polymerization yields and the molecular weights of polymers were investigated. Water soluble polyacrylamides containing mercaptosuccinic acid end groups were synthesized. Such water soluble polymers prepared with Ce(IV)-organic reducing agent redox system containing amino, hydroxyl, carboxylic and thiol functional groups or end groups seem to be potential sources for the construction of high molecular weight polymers that can be destroyed under physiological conditions due to weakly bound structures occurring in the polymer and to have potential for the preconcentration and separation of some trace elements [24–28].

2. Experimental

Mercaptosuccinic acid(Merck), acrylamide(Merck), cerium(IV) sulfate(Merck) and sulfuric acid(Merck) were used without further treatment. Ce(IV) sulfate, mercaptosuccinic acid and acrylamide are denoted as Ce(IV), MSA and AAm respectively.

Polymerizations were carried out in a round-bottomed flask equipped with a stirrer by adding the calculated amount of Ce(IV) salt or KMnO$_4$ solution to aqueous solution of acrylamide monomer and mercaptosuccinic acid. The oxidants (cerium(IV) sulfate and potassium permanganate) were dissolved in the calculated amount of sulfuric acid solution. The solution volume containing oxidant was kept constant at 20 ml. The total volume of polymerization solution was 100 ml. It was

reported that H$_2$SO$_4$ was used to increase the solubility of the oxidant and to prevent the hydrolysis of the oxidant. Moreover, the redox reaction between mercaptosuccinic acid and Ce(IV) or KMnO$_4$ salt takes place in acetic medium [1–22, 30–34]. After polymerization was completed, the solution was poured into an excess of acetone to precipitate the raw polymer. In the precipitation of polymers in acetone, volume ratios of acetone to polymer solution were exactly 7/1. The weight of isolated polymer was determined by direct weighting of polyacrylamide dried in air and the yield % was calculated by using Equation (1).

$$\text{Yield}\,[\%] = \frac{\text{weight of isolated polymer}\,[\text{g}]}{\text{weight of monomer}\,[\text{g}]}\cdot 100 \quad (1)$$

In polymerization reaction, the effects of the initiator concentration ($C_{Ce(IV)} = 1.4\cdot 10^{-3}$, $2.8\cdot 10^{-3}$, $7\cdot 10^{-3}$, $14\cdot 10^{-3}$ and $20\cdot 10^{-3}$ mol/l) at different acid concentrations, the temperature ($T = 20, 30, 40, 50$ and $60°C$), polymerization time ($t = 5, 10, 30$ and 60 minutes) and the concentration of sulfuric acid ($C_{H_2SO_4} = 0.05, 0.10, 0.20$ and 0.40 mol/l) on the yield and molecular weight were examined. The $n_{Ce(IV)}/n_{MSA}$ ratio was kept constant at 1.

It seems from previous investigations, that the formation of radicals on carboxyl groups may be possible [2, 33]. However, the probability of radical formation on carboxyl groups may appear less than that of other radical formation reactions given in Figure 1, due to the formation of acid (proton) influence. It was also described that the redox reactions in the use of thioglycolic acid and 3-mercap-
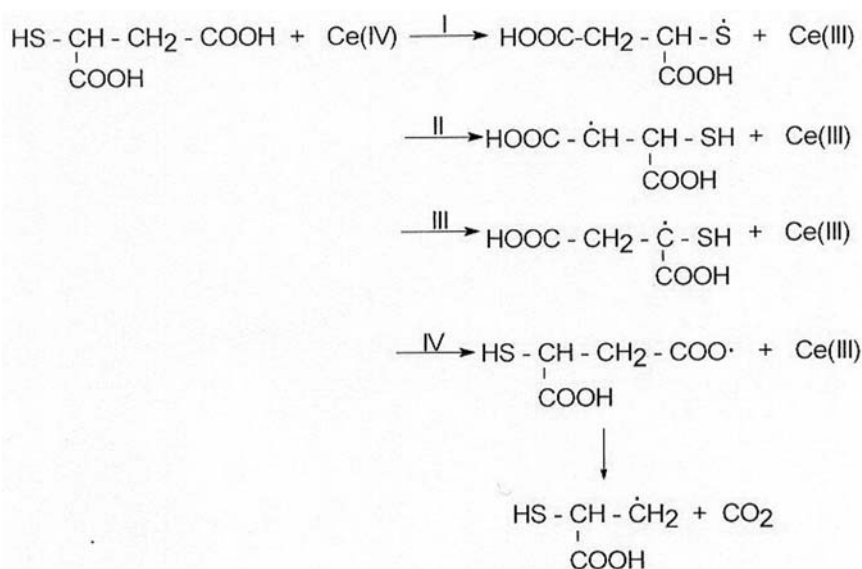

Figure 1. Radical formation reactions occurring between mercaptosuccinic acid and Ce(IV) ions
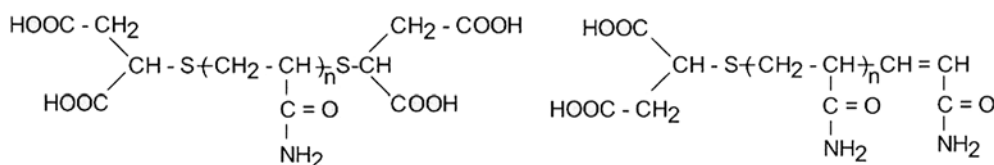
Figure 2. Probable structures of the synthesized polymers

topropionic acid as reducing agents in the redox systems occur at lower temperature, due to low bonding energy of S–H bond [30, 34].

The radical generation is believed to occur by one electron transfer from mercaptosuccinic acid to Ce(IV) according to the reactions given in Figure 1 as reported in the literature [22, 30, 34].

Because of low S–H bonding energy, the formation of free radicals in reaction I in Figure 1 is more likely than other reactions to initiate polymerization of acrylamide and oxidative termination of polymer radicals is also possible by ceric ions [2, 22, 30, 33–36]. For this reason, in the polymerization reaction, water soluble polyacrylamides having more probable structures given below in Figure 2 have been obtained.

Infrared measurements were carried out with ATI Unicam (Mattson 1000) FT-IR spectrometer and the spectra of polymers were determined by KBr disk method. For this purpose, pallets of about 300 mg KBr powder containing finely grained powder of MSA, AAm or PAAm sample(7–8 mg) were made. The FT-IR spectra of MSA, AAm and PAAm synthesized using MSA-Ce(IV) redox system were recorded by ATI Unicam (Mattson 1000) FT-IR spectrometer.

For determination of the viscosity average molecular weight (M_v), the flow time of dilute solution of polyacrylamide with 0.5 g/dl and that of water (the average value of flow times for three measurements was 163±0.2 s for water at 30°C) was measured by an Ubbelohde-level viscometer at 30°C. The intrinsic viscosities (|η|) of polymer solutions were calculated by using Equation (2) [29–30].

$$|\eta| = \frac{\eta_{sp} + 3\ln(\eta_r)}{4C} \tag{2}$$

The relative(η_r) and specific(η_{sp}) viscosities were calculated using Equations (3) and (4).

$$\eta_r = \frac{t}{t_0}; \quad \eta_{sp} = \frac{t - t_0}{t_0} = \eta_r - 1 \tag{3), (4}$$

t_0 and t are the flow times of water and polymer solution of defined volume in Ubbelohde capillary viscometer.

In standard measurements, the solution viscosity is measured in at least three different concentrations and triplicates for extrapolation of the Huggins or Kraemer plots to infinite dilution. However, this method is quite laborious and time consuming.

The molecular weights of polymers were determined by the Mark-Houwink equation (5).

$$|\eta| = K\,M_v^{\alpha} \tag{5}$$

Where K and α are constants which are dependent on the solvent, type of polymer and the temperature of system. For polyacrylamide aqueous solution at 30°C, the values of K and α are $6.88 \cdot 10^{-4}$ and 0.66 respectively.

The UV measurements (200–1000 nm) were done using a JASCO V-530 UV/VIS spectrometer equipped with a temperature control attachment.

For fluorescence measurement, PTI QM-4/2003 spectrofluorimeter was used to establish the presence of Ce(III) in the polymer. 75 watt xenon lamp was operated at an excitation wavelength of 260 nm and a slit width of 1 nm

An Analytik Jena Vario 6 AAS, flame atomic absorption spectrometer was used for determining Mn(II) in polymers. Manganese hallow cathode lamps were operated at a wavelength of 297.5 nm and a slit width of 0.2 nm.

3. Result and discussion

In the polymerization of acrylamide initiated by Ce(IV)- mercaptosuccinic acid or KMnO$_4$-mercaptosuccinic acid in acid-aqueous medium, the formation radicals of –S˙ is energetically most favorable due to low S–H bonding energy. Therefore the polymerization of acrylamide initiated with Ce(IV)-organic reducing agents such as polyamino, amino and carboxylic acids [17–22] requires higher energy, longer time and lower acid concentration

than that initiated with Ce(IV)-organic reducing agents containing thiol groups.

The effect of initiator concentration at different acid concentrations ($C_{H_2SO_4}$ = 0.05, 0.10 and 0.20 mol/l) on the molecular weight of polymer and the yield are shown in Figure 3 and 4 respectively. The increase in the initiator concentration at a constant monomer concentration of 0.7 mol/l resulted in a decrease in molecular weight (Figure 3) but an
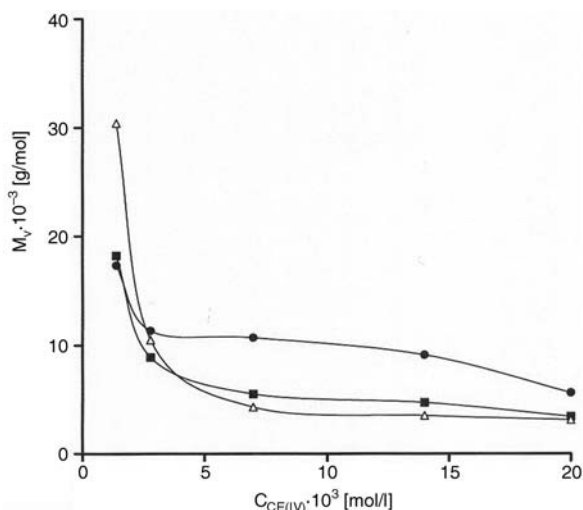
increase in the yield (Figure 4) of polymer which contains mercaptosuccinic acid end-groups.

The increase of the temperature in the polymerization reaction resulted in an increase in the molecular weight of polymer and slight decrease in the yield of polymer (Figure 5). This unexpected result must be because of the side reactions of the primary radicals generated from mercaptosuccinic acid. Those side reactions might be recombination of the initiating primary radicals or any other radical addition to the amide carboxyl etc. Similar unusual behavior has been reported by Lozinsky *et al.* [32] in the polymerization of polyacrylamide initiated with tertiary amine-persulfate redox couple.

The dependence of the yield and molecular weight of polymer on the acid concentration at different

Figure 3. The effect of the initiator concentration on the molecular weight of polymer synthesized by using mercaptosuccinic acid-Ce(IV) redox system at different acid concentrations. $C_{H_2SO_4}$ = 0.05(●), 0.1(■) and 0.2(△). C_{AAm} = 0.7 mol/l; T = 30°C; t = 10 min; $n_{Ce(IV)}$ = n_{MSA}

Figure 5. The effect of the temperature on the yield and molecular weight of polymer. C_{AAm} = 0.7 mol/l; $C_{Ce(IV)}$ = 7·10⁻³ mol/l; $n_{Ce(IV)}$ = n_{MSA}; $C_{H_2SO_4}$ = 0.05 mol/l; t = 10 min

Table 1. The dependence of the yield and the molecular weight of polymer on the acid concentration and the polymerization time. C_{AAm} = 0.7 mol/l; T = 30°C; $n_{Ce(IV)}$ = n_{MSA}

$C_{Ce(IV)} \cdot 10^3$ [mol/l]	$C_{H_2SO_4}$ [mol/l]	Polymerization time [min]	Yield [%]	M_v [g/mol]
7.0	0.05	10	62,0	9 400
7.0	0.10	10	57.9	5 500
7.0	0.20	10	40.7	4 300
7.0	0.40	10	66.6	6 450
2.8	0.05	10	21.1	11 350
2.8	0.10	10	32.1	8 900
2.8	0.20	10	37.8	10 500
2.8	0.40	10	52.9	17 600
7.0	0.05	5	62.7	8 650
7.0	0.05	30	74.9	8 500
7.0	0.05	60	64.2	8 100

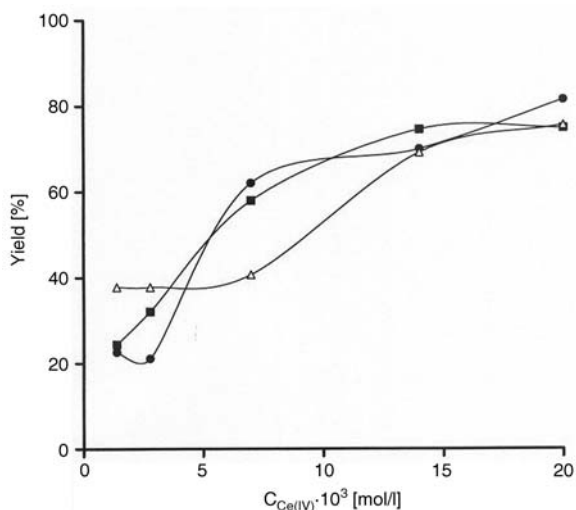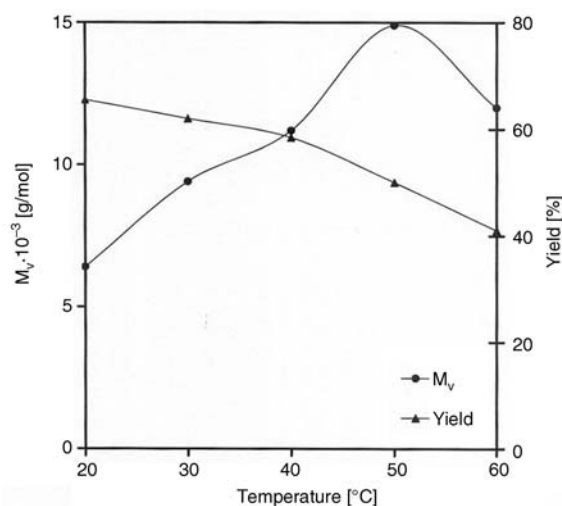**Figure 4.** The dependence of polymerization yield on the initiator concentration at different acid concentrations. $C_{H_2SO_4}$ = 0.05(●), 0.1(■) and 0.2(△). C_{AAm} = 0.7 mol/l; T = 30°C; t = 10 min; $n_{Ce(IV)}$ = n_{MSA}

initiator concentrations and the polymerization time is shown in Table 1. When examining Figure 3 and Table 1, it is seen that the increase in the acid concentration resulted in a decrease in the molecular weight of polymer at higher Ce(IV) concentration. However, at low Ce(IV) concentration, with increasing acid concentration, the molecular weight of polymer increased. No significant change was observed in the molecular weights by extension of polymerization time. Polymerization yield remains constant at around 62–64.2% except for 74.9% of polymerization yield at 30 minutes of polymerization time. We attributed this phenomenon to an oxidation-reduction reaction between mercaptosuccinic acid and oxidant which was completed rapidly during a few minutes in the polymerization of acrylamide monomer in acid-aqueous medium. It was also observed that both colors of oxidants (Ce(IV) and $KMnO_4$) in polymerization reactions disappeared rapidly when their adding were completed.

To determine the acid values of PAAm with carboxyl end-groups synthesized at different initiator concentrations and at constant sulfuric acid concentration(0.10 mol/l), 0.3 g of each polymer was dissolved in distilled water and the total solution volume was 50 ml. The solutions of these polymer containing different amounts of mercaptosuccinic

acid as carboxyl end-groups were titrated with 0.1 N NaOH solution by conductometric titration. The titration curves of polymer solutions containing different amounts of mercaptosuccinic acid as end-group by using 0.1 N NaOH solution as titrant were shown in Figure 6. The initial conductivities of polymer solutions, the amount of volume of 0.1 N NaOH solution at neutralization point in titration reaction and the calculated acid values of acrylamide polymers synthesized at various initiator concentrations in the polymerization reactions were given in Table 2. As can be seen from Table 2, the initial conductivities of polymer solutions and acid values of polymers indicated an increase with augmentation of mercaptosuccinic acid in different redox systems at constant sulfuric acid concentration (0.10 mol/l) in polymerization reactions. These results support the idea that polymers synthesized by using of mercaptosuccinic acid as a reducing agent in different redox systems contain carboxyl end-groups

The UV spectrum of polyacrylamide obtained using Ce(IV)-organic acid or amino acid (with or without thiol group) redox system indicates generally a peak at 254 nm, due to the complex formation between Ce(III) ions and polymer containing reducing agent as end-groups [21–23]. Two peaks at 238 nm and 254 nm were observed in the UV spectrum of acrylamide polymer synthesized using mercaptosuccinic acid –Ce(IV) redox system (Figure 7). It was reported that similar peaks at 238 and 253 nm were obtained in the UV-Visible spectra of polyacrylamides synthesized using Ce(IV)-thioglycolic acid redox system [30]. The obtained spectrophotometric data from peak values at 238 and 254 nm in Figure 5 and the values of Ce(IV) concentrations in polymerization reactions have been listed in Table 3. As can be seen from Figure 5
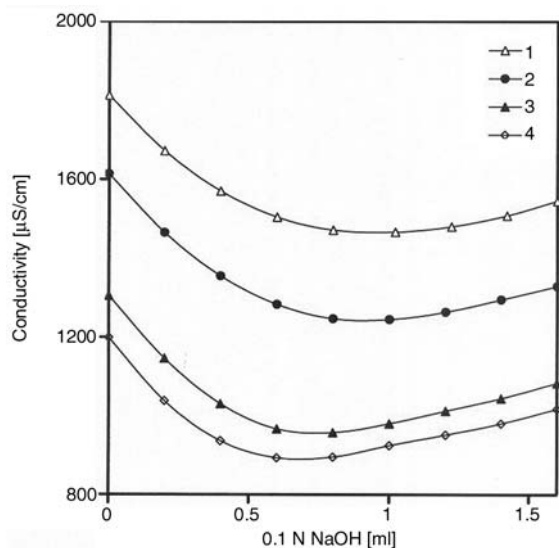

Figure 6. The conductometric titration curves of polymer solutions(0.3 g polymer/50 ml solution in distilled water) obtained at various initiator concentrations. $C_{Ce(IV)} = 20 \cdot 10^{-3}(1)$, $14 \cdot 10^{-3}(2)$, $7 \cdot 10^{-3}(3)$ and $2.8 \cdot 10^{-3}(4)$. $C_{AAm} = 0.7$ mol/l; $C_{H_2SO_4} = 0.1$ mol/l; $T = 30°C$; $t = 10$ min; $n_{Ce(IV)} = n_{MSA}$

Table 2. Initial conductivities of polymer solutions(0.3 g polymer/50 solution in water) and acid values of polyacrylamides containing mercaptosuccinic acid end groups synthesized at different initiator concentrations. $C_{AAm} = 0.7$ mol/l; $C_{H_2SO_4} = 0.1$ mol/l; $T = 30°C$; $t = 10$ min; $n_{Ce(IV)} = n_{MSA}$

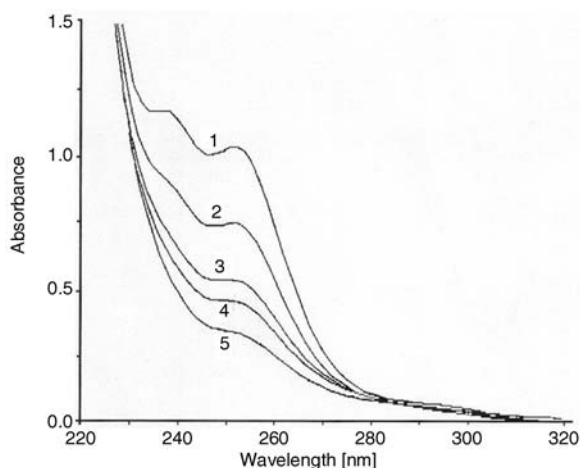| $C_{Ce(IV)} \cdot 10^3$ [mol/l]	Initial conductivities of polymer solution [μS/cm]	V_{NaOH} [ml]	n_{COOH} [mmol/g polimer]
20.0	1813	0.62	0.206
14.0	1614	0.58	0.193
7.0	1305	0.52	0.173
2.8	1199	0.45	0.150

Figure 7. The dependence of absorbance values of polymer solution($C_{polimer}$ = 0.25 g/100 ml solution in water) on the initiator concentration in polymerization reaction. $C_{Ce(IV)}$ = $20 \cdot 10^{-3}$(1), $14 \cdot 10^{-3}$(2), $7 \cdot 10^{-3}$(3), $2.8 \cdot 10^{-3}$(4) and $1.4 \cdot 10^{-3}$(5); C_{AAm} = 0.7 mol/l; $C_{H_2SO_4}$ = 0.1 mol/l; T = 30°C; t = 10 min; $n_{Ce(IV)}$ = n_{MSA}

Table 3. The relation between the absorbance values of polymer solutions ($C_{polimer}$ = 0.25 g polymer/ 100 ml solution in water) measured at 238 nm and 254 nm and the initiator concentration in polymerization reaction at 30°C. C_{AAm} = 0.7 mol/l; $C_{H_2SO_4}$ = 0.1 mol/l; $n_{Ce(IV)}$ = n_{MSA}

$C_{Ce(IV)} \cdot 10^3$ [mol/l]	Absorbance values at 254 nm	Absorbance values at 238 nm
20.0	1.013	1.168
14.0	0.733	0.908
7.0	0.523	0.714
2.8	0.466	0.640
1.4	0.332	0.561

and Table 3, the decrease in the initiator concentration in the polymerization reaction led to a decrease in the absorbance values of polyacrylamide solutions (0.25 g polymer/100 ml solution in water) at 238 nm and 254 nm. Since, polyacrylamide itself does not represent any absorption within this range, the observed adsorption bands indicates the presence of cerium(III) salt retention in free form or bonded to the polymer.

Unlike the fluorescence curve of homopolyacrylamide, the fluorescence curves of polyacrylamide obtained using mercaptosuccinic acid-Ce(IV) redox system show a peak at 351 nm (Figure 8). The peak values at 351 nm obtained from fluorescence curves of polymer solution indicated in Figure 8 and the values of different initiator concentrations in polymerization reaction were listed
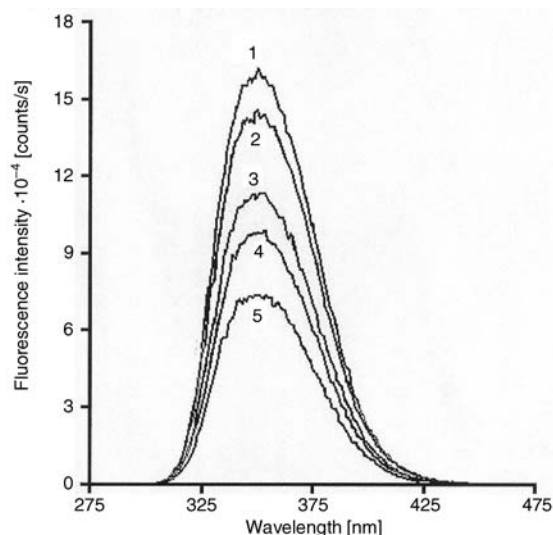

Figure 8. The fluorescence curves of polyacrylamide solutions($C_{polimer}$ = 0.25 g polymer/100 ml solution in water) synthesized at various initiator concentrations. $C_{Ce(IV)}$ = $20 \cdot 10^{-3}$(1), $14 \cdot 10^{-3}$(2), $7 \cdot 10^{-3}$(3), $2.8 \cdot 10^{-3}$(4) and $1.4 \cdot 10^{-3}$(5); excitation wavelength = 260 nm; slit width=1 nm; $C_{H_2SO_4}$ = 0.1 mol/l; C_{AAm} = 0.7 mol/l; T = 30°C; t = 10 min; $n_{Ce(IV)}$ = n_{MSA}

Table 4. The effect of the initiator concentration in the polymerization reaction on the fluorescence intensity of polymer solution ($C_{polimer}$ = 0.25 g polymer/ 100 ml solution in water; excitation wavelength = 260 nm; slit width = 1 nm) at 351 nm. $C_{H_2SO_4}$ = 0.1 mol/l; C_{AAm} = 0.7 mol/l; T = 30°C; t = 10 min; $n_{Ce(IV)}$ = n_{MSA}

$C_{Ce(IV)} \cdot 10^3$ [mol/l]	Fluorescence intensity $\cdot 10^{-4}$ at 351 nm [counts/s]
20.0	15.93
14.0	14.24
7.0	11.34
2.8	7.56
1.4	7.38

in Table 4. It was observed that with increasing Ce(IV) content in the polymerization reaction, the fluorescence intensity of polymer solution (0.25 g polymer/100 ml solution in water) at 351 nm increased. Ce(IV) reduces to Ce(III) in polymerization reaction and this indicates that reduced Ce(III) ions are absorbed by the polymer.

The FT-IR spectra of acrylamide (AAm), mercaptosuccinic acid (MSA) and polyacrylamide (PAAm) containing mercaptosuccinic acid end-groups were given in Figure 9. As can be seen from Figure 9, the band at 3400 which can be assigned to symmetrical and asymmetrical stretching of N–H group
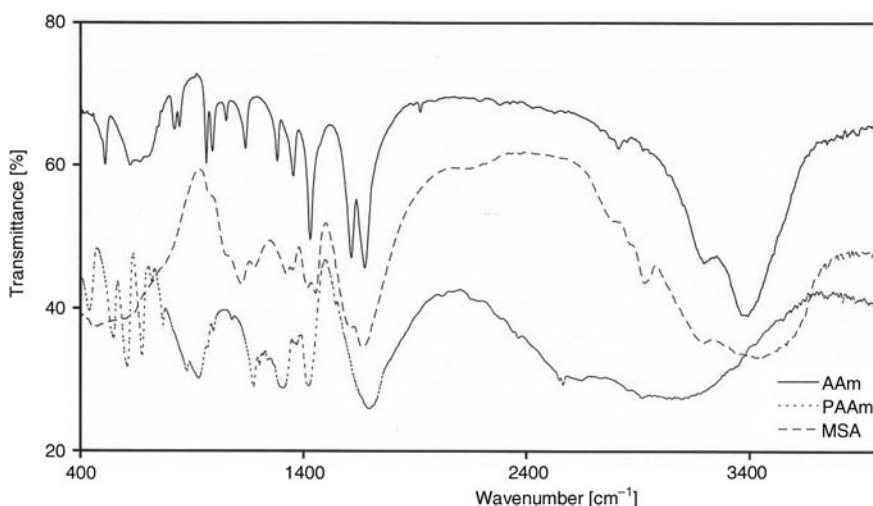
Figure 9. FT-IR spectra of acrylamide (AAm), mercaptosuccinic acid (MSA) and polyacrylamide (PAAm) obtained using mercaptosuccinic acid-cerium(IV) sulfate redox system
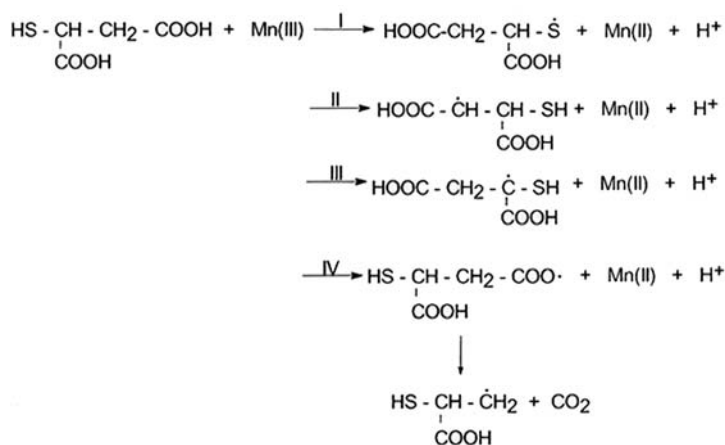

Figure 10. Radical generation reactions occurring between mercaptosuccinic acid and Mn(III) ions

observed in the FT-IR spectrum of acrylamide monomer was has been observed to shift to a band at 3450 cm^{-1} in the spectrum of polyacrylamide. The characteristic C=O stretching vibration bands of amide and acid groups have been observed at 1680 and 1720 cm^{-1} respectively. The peaks observed at 1620 cm^{-1} which have been attributed to the –CH=CH$_2$ group observed in the FT-IR spectrum of acrylamide monomer disappeared in the FT-IR spectrum of polyacrylamide. The band at 1430 cm^{-1} indicates O–H bending, the existence of C–O stretching in the plane of C–O–H bending in mercaptosuccinic acid and N–H stretching in acrylamide and polyacrylamide. There are also peaks at 1280 and 1180–1190 cm^{-1} which are seen in the FT-IR spectra of acrylamide and polyacrylamide. These peaks belong to N–-H stretching of amide groups in acrylamide and O–H bending respectively which are observed in the FT-IR spectra of mercaptosuccinic acid and polyacrylamide contain-

ing mercaptosuccinic acid end-groups. Moreover the peaks in the spectrum presented for polyacryamide can arise due to metal ions absorbed in the polymer.

Potassium permanganate in spite of being a powerful and versatile oxidant is incapable of initiating vinyl polymerization by itself in dark. If, however, the polymerization medium is sufficiently acidic to dissolve the manganese dioxide produced by the interaction of vinyl monomer with permanganate, polymerization can be initiated by adding reducing agent and manganese dioxide dissolves in carboxylic or hydroxyl carboxylic acids, producing highly reactive Mn(III) ions [2, 33]. Both Mn(IV) and Mn(III) ions formed can be react with mercaptosuccinic acid to produce radicals for the polymerization of acrylamide monomer in acid-aqueous medium. The radical generation mechanism in this redox reaction occurring between Mn(III) ions and mercaptosuccinic acid can be given as in Figure 10.

As explained in the mercaptosuccinic acid-Ce(IV) redox reaction defined in this paper, the formation of free radicals given in the reaction I of Figure 10 is more probable than other reactions to initiate polymerization of acrylamide monomer, due to low S–H bonding energy. As described in previous investigations, oxidative termination of polymeric radicals is also possible by Mn(III) or Mn(IV) ions [2, 22, 30, 33–36] and polyacrylamides having chemical structures given in Figure 2 can be obtained in the polymerization of acrylamide monomer initiated with KMnO$_4$-mercaptosuccinic acid redox system in acid aqueous medium.

Using mercaptosuccinic acid-KMnO$_4$ redox system, polymerization of acrylamide monomer was performed at different initiator concentrations at 30°C. It was observed that the increase of potassium permanganate concentration in polymerization reaction resulted in an increase in the yield but a decrease in molecular weight of polymer

Table 5. The effect of the initiator concentration on the yield and molecular weight of acrylamide polymer. $C_{H_2SO_4}$ = 0.05 mol/l; C_{AAm} = 0.7 mol/l; T = 30°C; t = 15 min

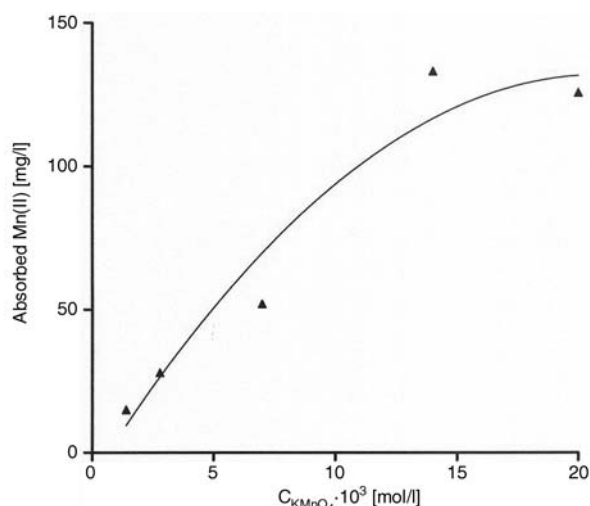| $C_{KMnO_4} \cdot 10^3$ [mol/l]	Yield [%]	M_v [g/mol]
1.4	18.1	56 600
2.8	25.6	26 800
7.0	36.6	12 850
20.0	37.6	8 000

Figure 11. The relation between the concentration of Mn(II) bounded to polymer and the initiator concentration at the beginning of polymerization reaction. T = 30°C; t = 10 min; C_{AAm} = 0.7 mol/l; $C_{H_2SO_4}$ = 0.05 mol/l; n_{KMnO_4} = n_{MSA}, $C_{polimer}$ = 0.25 g/dl

(Table 5). It is reported that manganese dioxide is produced by the interaction of vinyl monomer with permanganate and then manganese dioxide dissolves in acid producing highly reactive Mn(III) ions [2, 33]. Both Mn(IV) or Mn(III) ions reduced to Mn(II) ions during the polymerization reaction. The Mn(II) species that occur at the end of polymerization reaction are absorbed by the polymer [20–22]. The dependence of the concentration of Mn(II) which is incorporated into the polymer on the initiator concentration in the polymerization reaction is given in Figure 11. It is seen that the amount of Mn(II) bound to the polymer changes with the initial concentration of permanganate.

4. Conclusions

In this study, the effects of temperature, polymerization time, sulfuric acid concentration and initiator concentration on the yield and molecular weight of polymer were investigated. The results indicate that this redox system is very convenient to initiate acrylamide polymerization at room temperature. The polymerization of acrylamide using mercaptosuccinic acid-Ce(IV) or KMnO$_4$ redox system in acid aqueous medium was performed at room temperatures. In the polymerization of acrylamide initiated by Ce(IV)- mercaptosuccinic acid or KMnO$_4$-mercaptosuccinic acid redox system in acid-aqueous medium, the formation radicals of –S$^·$ is energetically most favorable due to low S–H bonding energy. As a result, mercaptosuccinic acid is a convenient radical source for generation of radicals to initiate acrylamide polymerization at room temperature.

References

[1] Launer H. F., Yost D. M.: The kinetics of the reaction between potassium permanganate and oxalic acid. Journal of the American Chemical Society, **56**, 2571–2577 (1934).

[2] Misra G. S., Bajpai U. D. N.: Redox polymerization. Progress in Polymer Science, **8**, 61–131 (1982).

[3] Narita H., Maghida S.: The polymerization of acrylamide initiated with ceric ion. Die Angewandte Makromolekulare Chemie, **97**, 209–215 (1966).

[4] Pramanik D., Chaterjee A. K.: Mechanistic studies on ceric-thiourea-initiated polymerization in acid aqueous media from end group analysis. Journal of Polymer Science Part A-Polymer Chemistry, **18,** 311–319 (1980).

[5] Özeroglu C., Yalçinyuva T.: Oxidative polymerization of methyl methacrylate in acid-aqueous medium. Polymer-plastics Technology and Engineering, **43**, 731–743 (2004).

[6] Biçak N., Özeroglu C.: Low temperature initiation by methylene bis(diethyl malonate)-Ce(IV) redox system in organic solvents. European Polymer Journal, **37**, 2393–2395 (2001).

[7] Sui K. Y., Gu L. X.: Preparation and characterization of amplihilic block copolymer of polyacrylonitrile-block-poly(ethylene oxide). Journal of Applied Polymer Science, **89**, 1753–1759 (2003).

[8] Saraç A. S., Özkara. Ş., Ustamehmetoglu B., Sezer E.: Controlled electroinduced polymerization of methyl meyhacrylate in the presence of catalytic amount of Ce(IV). Journal of Macromolecular Science Part A: Pure and Applied Chemistry, **40**, 193–207 (2003).

[9] Ananthanarayanan V. S., Santappa M.: Kinetics of vinyl polymerization initiated by ceric ion in aqueous solution. Journal of Applied Polymer Science, **9**, 2437–2447 (1965).

[10] Mino G., Kaizerman S., Rasmussen E.: The polymerization of acrylamide initiated by ceric nitrate-3-chloro-1-propanol redox system. Journal of Polymer Science, **38**, 393–401 (1959).

[11] Subramaniun S. V., Santappa M.: Vinyl polymerization initiated by ceric ion-reducing agent system in sulfuric acid media. Journal of Polymer Science Part A-Polymer Chemistry, **6**, 493–504 (1968).

[12] Palit S. R., Konar R. S.: Permanganate-oxalic acid as a initiator of acrylonitrile polymerization in aqueous media: (III) Kinetics and degree of polymerization. Journal of Polymer Science Part A-Polymer Chemistry, **2**, 1731–1748 (1964).

[13] Palit S. R., Konar R. S.: Permanganate-$H_2C_2O_4$ as an initiator in aquelus media: (II) The kinetics and degree of polymerization. Journal of Polymer Science, **58**, 85–102 (1962).

[14] Misra G. S., Narain H.: Aqueous polymerization of acrylic acid initiated by potassium permanganate-oxalic acid redox system. Die Makromoleculare Chemie, **113**, 85–94 (1968).

[15] Hussain M. M., Gupta A.: Effect of some additions on the aqueous polymerization of acrylamide initiated by permanganate-oxalic acid redox system. Die Makromoleculare Chemie, **178**, 29–36 (1977).

[16] Akar A., Öz N.: Low molecular weight poly(acrylic acid) with nitrilo di(methylenephosponic acid) chain ends for scale inhibition. Die Angewandte Makromolekulare Chemie, **273**, 12–14 (1999).

[17] Saraç A. S., Erbil C., Soydan A. B.: Polymerization of acrylamide initiated with electrogenerated cerium(IV) in the presence of EDTA. Journal of Applied Polymer Science, **44**, 877–881 (1992).

[18] Erbil C., Cin C., Soydan A. B., Saraç A. S.: Polyaminocarboxylic acids-Ce(IV) redox systems as an initiator in acrylamide polymerization. Journal of Applied Polymer Science, **47**, 1643–1648 (1993).

[19] Saraç A. S., Başak A. H., Soydan A. B., Akar A.: Polymerization of acrylamide by electrolytically generated Ce(IV)-organic acid redox system. Die Angewandte Makromolekulare Chemie, **198**, 191–198 (1992).

[20] Özeroglu C., Güney O., Saraç A. S., Mustafaev M. I.: The polymerization of acrylamide initiated with Ce(IV) and $KMnO_4$ redox systems in the presence of glycine. Journal of Applied Polymer Science, **60**, 759–765 (1996).

[21] Özeroglu C., Güney O., Mustafaev M. I.: Oxidative polymerization of acrylamide in the presence of L-threonine. Die Angewandte Makromolekulare Chemie, **249**, 1–9 (1997).

[22] Özeroglu C., Kurtoglu A. E.: The synthesis and characterization of acrylamide polymer containing R-(+)-cystein end groups. European Polymer Journal, **37**, 1053–1059 (2001).

[23] Ustamehmetoglu B., Diler Z. I., Saraç A. S.: Chemical polymerization of acrylamide initiated with Ce(IV)-dicarboxylic acid redox system: effect of chain length between the carboxyl groups. International Journal of Polymer Analysis and Characterization, **7**, 263–272 (2002).

[24] Saraç A. S., Özeroglu C., Mustafaev M. I.: The ternary complexes of bovine serum albumin and polyacrylamide derivatives in the presence of copper ions in neutral water. Journal of Bioactive and Compatible Polymers, **10**, 121–134 (1995).

[25] Özeroglu C., Namazova N., Mustafaev M. I., Saraç A. S.: The complex formation between polyacrylamide containing glycine end groups and bovine serum albumin in the presence of copper(II) in neutral aqueous water. Colloid and Polymer Science, **274**, 418–427 (1996).

[26] Petrov R. V., Mustafaev M. I., Norimov A. Sh.: Physicochemical criteria for the constraction of artificial immunomodulators and immunogens on the basis of polyelectrolyte complexes. Sov. Med. Rev. D. Immunol., pp. 1–13. Harwood Academic Publisher GmbH. London UK (1992).

[27] Özcan M., Akman S., Özeroglu C.: The use of water soluble polymers for the preconcentration and separation of copper, lead and chromium prior to their determination by graphite furnace atomic absorption spectrometry. Analytical Letters, **35**, 1075–1083 (2002).

[28] Özcan M., Akman S., Erbil C., Saraç A. S.: Determination of copper, chromium, manganese and zinc by graphite furnace atomic absorption spectrometry after separation on polyacrylamide modified with nitriloacetic acid. Fresenius' Journal of Analytical Chemistry, **355**, 665–666 (1996).

[29] Chuah H. H., Lin-Vien D., Soni U.: Poly(trimethylene terephthalate) molecular weight and Mark-Houwink equation. Polymer, **42**, 7137–7139 (2001).

[30] Özeroglu C., Erdogan S.: Oxidative polymerization of acrylamide in the presence of thioglycolic acid.

Central European Journal of Chemistry, **3**, 705–720 (2005).

[31] Tsubokawa N., Maruyama K., Sone Y., Shimomura M.: Graft polymerization of acrylamide from ultra silica particles by use of a redox system consisting of ceric ion and reducing groups on the surface. Polymer Journal, **21**, 475–481 (1989).

[32] Lozinsky V. I., Ivanov R. V., Kalinina E. V., Timofeeva G. I., Khoklov A. R.: Redox-initiated polymerization of acrylamide in moderately frozen water solutions. Macromolecular Rapid Communications, **22**, 1441–1446 (2001).

[33] Saraç A. S.: Redox polymerization. Progress in Polymer Science, **24**, 1149–1204 (1999).

[34] Özeroglu C., Özduganci C.: Low temperature initiation by 3-mercaptopropionic acid-Ce(IV) or -KMnO$_4$ redox system for polymerization of acrylamide monomer. Polymer-plastics Technology and Engineering, **45**, 549–554 (2006).

[35] Saha S. K., Chaudhuri A. K.: Effect of amines on ceric ion-initiated polymerization of vinyl monomers. II. Polymerization of acrylonitrile by ceric ion in the presence of various substituted amines. Journal of Polymer Science Part A-Polymer Chemistry, **10**, 797–808 (1972).

[36] Patra M., Sinha B. K.:Acrylamide polymerization initiated with the redox system Ce(IV)-cyclohexanone in miceller phase: A kinetic study. Macromolecular Chemistry and Physics, **199**, 311–317 (1998).